



A Sol-gel Membrane Utilized Cellulose Paper Doped with α -furyl Dioxime for Colorimetric Determination of Nickel

Muhammad B. Thohir¹ · Roto Roto² · Suherman Suherman² 

Received: 30 August 2022 / Accepted: 2 September 2022

© The Author(s), under exclusive licence to Springer Science+Business Media, LLC, part of Springer Nature 2022

Abstract

A simple and sensitive colorimetric sensor for nickel(II) ions has been successfully prepared by immobilizing α -furyl dioxime reagent in the sol-gel matrix with a solid supporting filter paper medium. The sensor was developed using tetraethyl orthosilicate (TEOS) precursors with 4 days aging time, the mole ratio of water: precursor was 4:1, and reagent concentration at 0.10%. The sensor was quantified by utilizing the Red (R), Green (G), and Blue (B) values of the colors that were successfully displayed after the detection process. The RGB value is confirmed by the Euclidean Distance (ED) equation to determine the optimum conditions. There was no observed degree of leaching in plain sight, and the result of leaching investigation by the double dyeing method did not show any significant change. The linear range was 0.10 to 2.8 ppm with an R^2 of 0.9964. The values of LOD and LOQ were 0.1 ppm and 0.4 ppm, respectively. In addition, the sensor was free from interfering species and had a percent recovery around 90 to 110%.

Keywords Sensor · Nickel(II) ions · Sol-gel · α -furyl dioxime · RGB

Introduction

Nickel has been utilized for biological processes such as respiration, biosynthesis, and metabolism [1–2]. However, some adverse effects will arise when nickel amounts are out of normal range, such as asthma, dermatitis, pneumonia, and cancer [3–4]. Therefore, monitoring nickel-metal levels is urgently needed. Nickel metal analysis is commonly carried out using conventional AAS, ICP-MS, and XRF (Ghaedi et al. 2007; Milne et al. 2010; Herreros-Chavez et al. 2019). Various studies showed that the analysis results with those instruments have excellent sensitivity, selectivity, and %RSD value. However, the methods require considerable energy consumption; and many of these instrumental techniques require pre-treatments, additional reagents, and

complex preparations. This is in contrast to the 12 principles of green chemistry, so creating and modifying real-time analytical methods in the form of sensors becomes an urgent need nowadays (deMarco et al. 2018).

Sensors take various approaches, generally based on the interaction between the sensor and the reagent or the analyte. Optical sensors are based on observing the interaction between the sensor and analytes that changed the color of the sensor. The principle underlying detection in optical sensors is colorimetry. Colorimetry works based on changes in wavelength and intensity when reagents and samples interact (Gilchrist and Nobbs 2017). Due to colorimetry sensor is based on the liquid-solid reaction, so the sensors always need reagents that can survive both in liquid and solid media. In addition, the sensor also requires a solid supporting material that can immobilize the reagent without reducing its activity in detection process (Mizuguchi et al. 2008).

Various matrices for optical sensors have been developed, including polymers, beads, and sol-gel with glass support materials [11–12]. However, some disadvantages of these matrix types are the need for instruments when quantifying the detection results, a complicated preparation process, a long-time synthesis process, and complicated operation procedures. The sol-gel is one of the matrices with vast

✉ Suherman Suherman
suherman.mipa@ugm.ac.id

¹ Chemistry Program, Faculty of Science and Engineering, Bojonegoro University, 62119 Kalirejo, Bojonegoro, Indonesia

² Department of Chemistry, Faculty of Mathematics and Natural Sciences, Universitas Gadjah Mada, Sekip Utara Kotak Pos 21 BLS, 55281 Yogyakarta, Indonesia

opportunities to develop considering its ease of synthesis results control (Du et al. 2013). Sol-gel would have a different yield character when synthesis precursors are varied. The ease of managing the characteristics of these results is widely used in various fields. As for sensor applications, sol-gel is expected to form silica nets capable of encapsulating reagents without leaching. The active site of the reagent remains active and does not prevent the reagent from interacting with the analytes (Shahamirifard et al. 2018a, b).

The colorimetry method could detect nickel using derived oxime functional group compounds, including α -furyl dioxime. The α -furyl dioxime has a pair of N atoms with lone pairs and can form a chelate bonding with nickel. The sensitivity level of α -furyl dioxime reaches a 1: 6,000,000 ratio of Ni to solvent (Soule 1925). This fact leads to the potential of α -furyl dioxime to be developed in the manufacture of Ni(II) metal ion sensors. The sol-gel usage as a matrix for reagent immobilization can be applied to the solid supporting media in filter paper. The data obtained is measured by the RGB value, converted into the Euclidean Distance (ED) data (Feng et al. 2011). Therefore, it is possible to create a sensor with good sensitivity and easy quantification based on the data.

Experimental Section

Material

Chemicals were analytical grade from Merck, including tetraethyl orthosilicate (TEOS), methanol (MeOH), triton X-100 as a nonionic surfactant, hydrochloric acid (HCl), standard solutions of nickel, calcium, magnesium, copper, cobalt, zinc, lead, and ammonia solution (NH₃). Distilled water was obtained from Ikapharmindo Putramas, α -furyl dioxime was from Tokyo Chemical Industry, and Whatman 42 paper was acquired from GE Healthcare.

Instrument

A scan engine (Canon CanoScan LiDE 300) was used to record the results of detection, an infrared spectrophotometer (FTIR Thermo Nicolet iS10) for determination of functional groups, and a Scanning Electron Microscope (JEOL JSM- 6510LA) for assessment of the morphology of filter paper before and after detection. All instrumentation analysis were for three-time samples replication ($n=3$).

Preparation of sol-gel Matrix as a Ni(II) Ion Sensor

2 mL of TEOS and methanol mixture were sterilized for 30 min. Later, 694 μ L H₂O, 10 drops of Triton X-100, 2 mL

of reagent α -furyl dioxime 0.1%, and 0.5 M HCl of 0.5 mL were added dropwise to the mixture. The mix was stirred for 5 h. Furthermore, 1 cm \times 1 cm filter paper was immersed in a sol solution and allowed to stand for 24 h in a room without light to occur the process of hydrolysis and condensation of sol-gel in the filter paper pores. The filter paper was drained and left for 4 days for the aging wet gel. Before use, the synthesized sensor is heated at 40 °C. All sol-gel preparation processes were analyzed by one-way analysis of variation with the number of replicates adjusted for the number of variations.

Experimental Procedure for the Determination of Nickel

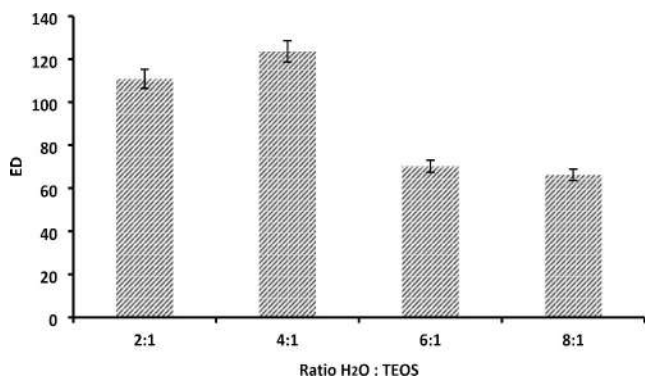
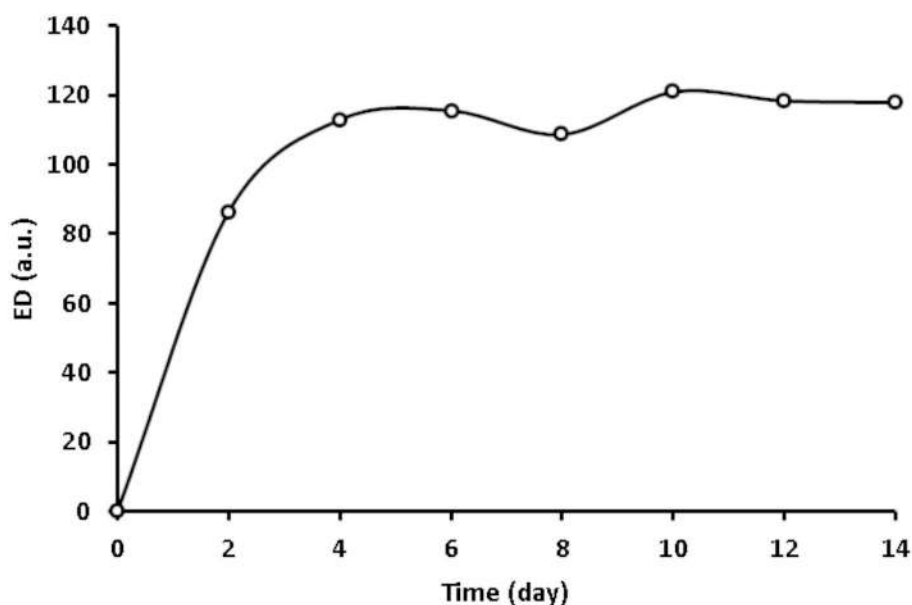
A nickel analyte with a concentration of 2 ppm was prepared as much as 10 mL. 0.5 mL of 2 M ammonia solution was added to the analyte. The sol-gel membrane was dipped in the analyte for 3 min to form a color. After the sensing process, the formed color is scanned to record the color change. By using the Euclidean Distance (ED) equation, the RGB value of the color is converted to the ED value. This step was also used for real samples (river and tap water) which taken from nature that have been acid-preserved.

In this study, testing of the degree of leaching and interference were conducted as well. The degree of leaching was carried out by contacting the sol-gel membrane with aquadest, after drying it was then contacted with nickel analyte. Meanwhile, the interference test was carried out by contacting the sol-gel membrane with 2 ppm nickel solution which had been added with various interference metals. The solution mixture was first alkalized with ammonia solution before being contacted.

Results and Discussion

Effect of Variations on Preparation Parameters Towards the Performance of Sensing

Each parameter given in the sol-gel synthesis will affect the structure of the synthesis product, such as stiffness, average pore size, pore size distribution, surface area, surface polarity, ionic conductivity, silanol functional group concentration, and structural properties of xerogel (Podbielska et al. 2006). The aging time is an affecting parameter towards the structural character and mechanical strength of the synthesis results. The aging process is the stage that separates the shape of the sol into a wet gel. At this stage, there will be a change in the structure of silica from Si-OH hydrolysis to Si-O-Si (Hench and West 1990). This stage

Fig. 1 The effect of aging time on ED values**Fig. 2** The effect of water: precursor ratio on ED value

is slow and will have consequences for the length of time needed for the aging stage to complete.

Silica sol could fill the pores of filter paper. This condition is different compare to glass media that utilize interactions between glass surfaces filled with silanol groups that expect interaction between the glass surface and silica sol (Samadi-Maybodi et al. 2015). In addition, the pores of glass are also much smaller than paper, considering a physical interaction occurred. In contrast, the gel filter paper matrix that has formed Si-O-Si filled the pores of filter paper without forming chemical bonds or other interactions with the surface of the supporting media so that the aging time needed for the sol-gel with filter paper media is much shorter than the glass media that require 14 days. Fact that a gel was formed is confirmed by SEM analyses.

Figure 1 shows that there was a sharp increase in intensity immediately on the 2nd day and continued on the 4th day, and appeared constant afterwards to the 14th day. This

data shows that with paper media, sol-gel has reached a good aging time even though it is only 2 days. It is very different from sol-gel which is embedded in glass media which requires aging time up to 14 days (Samadi-Maybodi et al. 2015).

The mole ratio of water and precursor is the most critical variation variable and is very influential on the results of sol-gel synthesis (Fig. 2). Increasing the water mole ratio resulted in more compounds that will play a role in converting Si-OR to Si-OH and allowing the alkoxysilan hydrolysis process to run more optimally. In other words, an increasing amount of alkoxysilane would be hydrolyzed and implicate in a growing number of Si-OH species which continue in the polymerization stage and form Si-O-Si. The ever-increasing number of moles of water in sol-gel synthesis also affected the speed of the hydrolysis process. Increasing the mole ratio of water will affect growing porosity and specific surface area. So the 4:1 mol ratio is the optimum condition of the sol-gel matrix in immobilizing reagents that produced optimum pores by α -furfuryl dioxymes (Dervin and Pillai 2017).

Determination of the optimum concentration is directly related to determining the maximum capacity of the matrix to encapsulate reagents. The small amount of reagent under the sensing range will decrease sensitivity, while the vast amount of reagent will stimulate the occurrence of leaching. The four variations of concentration did not affected on leaching, so it can be concluded that the sol-gel matrix had an encapsulation capacity reaching 0.1% of the added reagent (Fig. 3). The highest ED value indicated this condition.

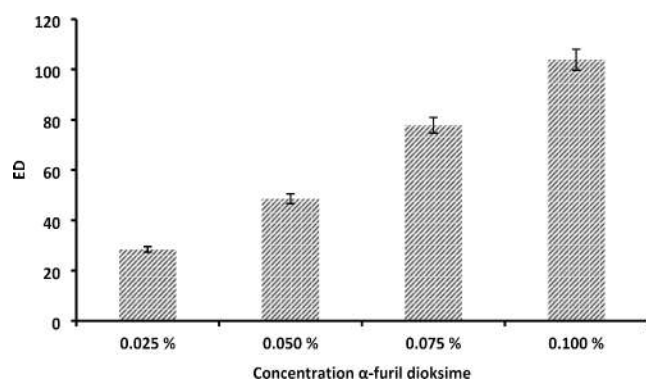


Fig. 3 The effect of reagent concentration on ED values

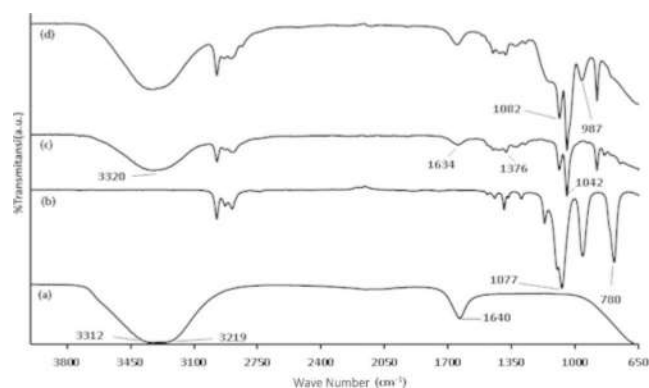


Fig. 4 IR spectra of the synthesis stage (a) H₂O (b) TEOS (c) α -furil dioximes (d) wet gel

Sensor Characterization

The FTIR spectra of H₂O showed three peaks with broad band intensity. In about 3200 cm⁻¹ there are two different peaks at 3312 cm⁻¹ and 3219 cm⁻¹, while one absorption appeared at 1640 cm⁻¹. The peak refers to asymmetric OH stretching vibrations, symmetry OH stretching vibrations, and OH bending vibrations, respectively. The IR spectra for TEOS showed several specific peaks for functional groups in TEOS compounds, such as peak at 1077 cm⁻¹ which are related to Si-O and C-O functional groups. This sharp shape of the peaks possibly due to domination of that groups in TEOS compounds (Choodum et al. 2015). Meanwhile, peak at 780 cm⁻¹ related to the vibration of -(CH₂)_n. The IR spectra for the α -furil dioxime reagent possessed on 1376 cm⁻¹, 1634 cm⁻¹, 1042 cm⁻¹, and 3320 cm⁻¹, which sequentially lead to symmetry stretching C=N, asymmetry stretching C=N, C-O-C stretch vibration, and -OH stretching vibration, respectively (Egneus 1972) (Fig. 4).

The spectra of the synthesized wet gel have an absorption profile that like the α -furil dioxime spectra, especially in specific areas of α -furil dioxime, such as absorption of about 1600 and 1300 cm⁻¹. In the wet gel spectra, the sol-gel results have characteristic an absorption peak at a

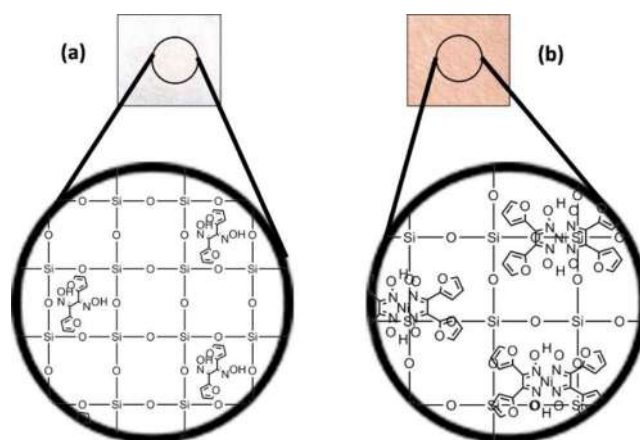


Fig. 5 Model of interaction (a) between xerogel and α -furil dioxime and (b) between xerogel and nickel- α -furil dioxime complex

wavenumber of 1082 cm⁻¹ indicating the absorption of Si-O. There is also a new peak at 987 cm⁻¹ which corresponds to Si-O-Si stretching; the intensity of these peaks was relatively small because, at the wet gel stage, the number of Si-O-Si chains formed was still relatively small. At the damp gel stage, there was no interaction between silica gel and the α -furil dioxime reagent; this was shown by the continued absorption of the active reagent groups at 1646 cm⁻¹ and 1379 cm⁻¹. So the interaction formed between the reagent and the matrix is only expected to be a physical interaction whose simulation is shown in Fig. 5.

Characterization of surface by using SEM was used to see the morphology of the filter paper of the solid supporting material before and after being coated with xerogel. As can be seen in Fig. 6a, the morphology of the filter paper has very large cavities and in Fig. 6b revealed that all cavities are covered by xerogel.

Degree of Leaching and Analytical Parameters

Determination of the degree of leaching is carried out by the twice-drying technique. Sensors free of leaching will show colors even if they have been contacted with distilled water. It means that the sensor does not lose its sensing quality due to leaching. In addition, Fig. 7 showed that the sensor surface which immersed in water first, then contacted with nickel, slightly decreased the ED value, but does not interfere with the sensing process and the difference is not detected by the eye.

The linear region will indicate the point of the concentration range resulting in the response, which is constantly increasing at the ED value obtained. Linearity data will show the y equation in Fig. 8. The y equation will also show the value of the slope, indicating the sensitivity of the synthesized sensor. While the LOD value obtained was 0.1 ppm, and the LOQ value was 0.4 ppm. These values are

Fig. 6 SEM images of Whatman 42 filter paper (a) before being coated with xerogel, and (b) after being coated with xerogel

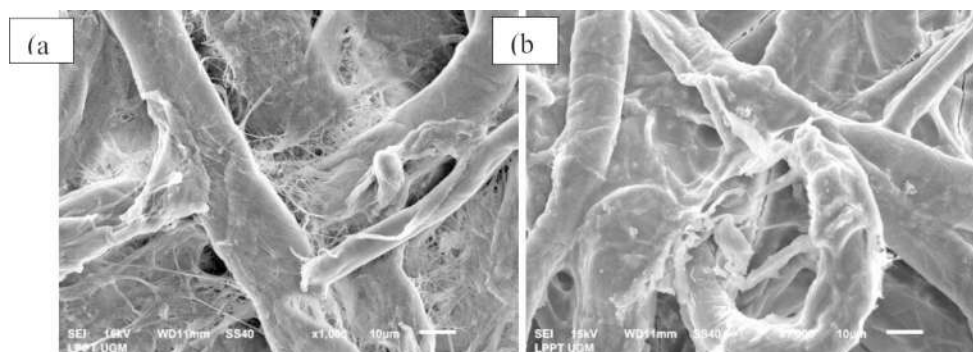


Fig. 7 Sensor leaching degree by double-dipping

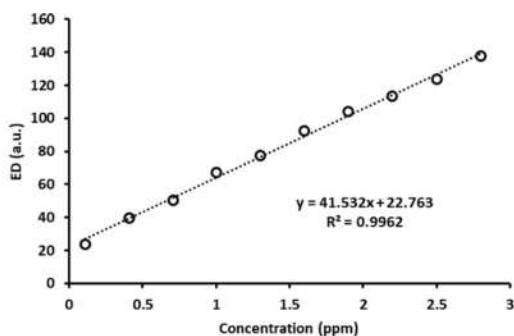
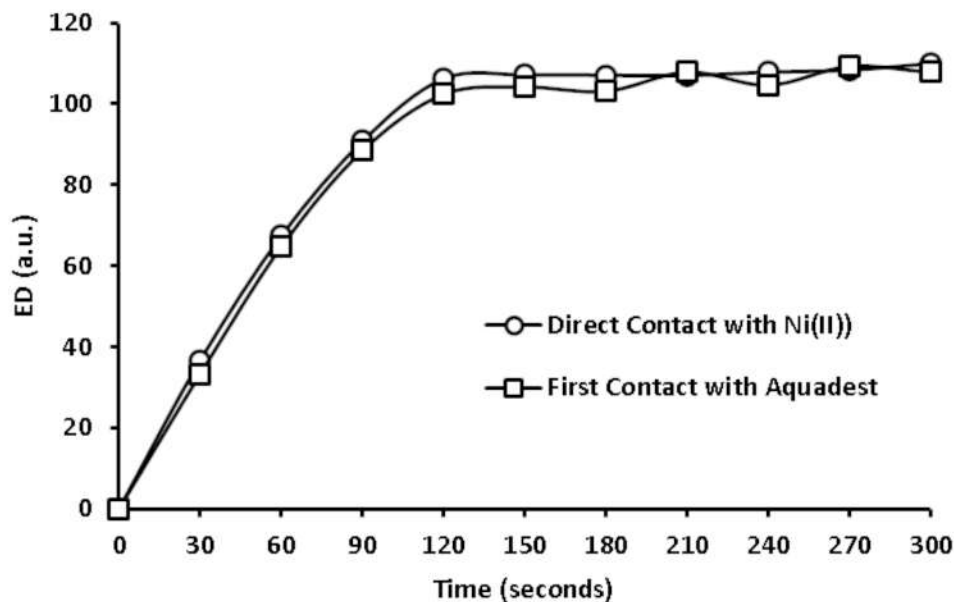


Fig. 8 Sensor standard curves and sensor color sequences

comparable with the previous results reported for nickel detection such as by modified UV-Vis method (Tokay 2017) and other methods [24–25].

The selectivity is a parameter that indicates the sensor's performance when contacted with environmental samples. Figure 9 showed that only Cr metal could significantly interfere with sensor performance among the tested metals. Based on the soft and hard acid-base theory, the metal ion of Cr(III) is classified as hard acid, and NH_3 is a hard base. Meanwhile, Ni(II) metal ion is classified as a borderline acid. Thus, NH_3 would prefer to interact with Cr(III) rather than Ni(II). However, this can be overcome by adding excess NH_3 so that there is still a Ni(II) and NH_3 complex that is formed even though Cr(III) metal is present.

Data on Fig. 9 expressed selectivity test results that the sensor can work with reasonable accuracy on environmental samples. Accuracy investigation will show the quality analysis from the proposed method, and the data is shown in Table 1. The method used to determine accuracy is spiking with 3 replications per sample. River and tap water samples have good % recovery results (which the origin concentration of nickel is around 2 ppm). Meanwhile, for the artificial samples with a concentration of 2 ppm, it is found that there

Wang L, Ye D, Cao D (2012) A novel coumarin Schiff-base as a Ni(II) ion colorimetric sensor. *Spectrochim Acta A* 90:40–44

Publisher's Note Springer Nature remains neutral with regard to jurisdictional claims in published maps and institutional affiliations.

Springer Nature or its licensor holds exclusive rights to this article under a publishing agreement with the author(s) or other rightsholder(s); author self-archiving of the accepted manuscript version of this article is solely governed by the terms of such publishing agreement and applicable law.

A Sol-gel Membrane Utilized Cellulose Paper Doped with α -furyl Dioxime for Colorimetric Determination of Nickel

by Muhammad B. Thohir .

Submission date: 06-Jun-2023 07:37PM (UTC+0700)

Submission ID: 2110271090

File name: BECT_published_2022.pdf (1.1M)

Word count: 3775

Character count: 19368



A Sol-gel Membrane Utilized Cellulose Paper Doped with α -fural Dioxime for Colorimetric Determination of Nickel

Muhammad B. Thohir¹ · Roto Roto² · Suherman Suherman²

2
Received: 30 August 2022 / Accepted: 2 September 2022

© The Author(s), under exclusive licence to Springer Science+Business Media, LLC, part of Springer Nature 2022

Abstract

A simple and sensitive colorimetric sensor for nickel(II) ions has been successfully prepared by immobilizing α -fural dioxime reagent in the sol-gel matrix with a solid supporting filter paper medium. The sensor was developed using tetraethyl orthosilicate (TEOS) precursors with 4 days aging time, the mole ratio of water: precursor was 4:1, and reagent concentration at 0.10%. The sensor was quantified by utilizing the Red (R), Green (G), and Blue (B) values of the colors that were successfully displayed after the detection process. The RGB value is confirmed by the Euclidean Distance (ED) equation to determine the optimum conditions. There was no observed degree of leaching in plain sight, and the result of leaching investigation by the double dyeing method did not show significant change. The linear range was 0.10 to 2.8 ppm with an R^2 of 0.9964. The values of LOD and LOQ were 0.1 ppm and 0.4 ppm, respectively. In addition, the sensor was free from interfering species and had a percent recovery around 90 to 110%.

Keywords Sensor · Nickel(II) ions · Sol-gel · α -fural dioxime · RGB

Introduction

Nickel has been utilized for biological processes such as respiration, biosynthesis, and metabolism [1–2]. However, some adverse effects will arise when nickel amounts are out of normal range, such as asthma, dermatitis, pneumonia, and cancer [3–4]. Therefore, monitoring nickel-metal levels is urgently needed. Nickel metal analysis is commonly carried out using conventional AAS, ICP-MS, and XRF (Ghaedi et al. 2007; Milne et al. 2010; Herreros-Chavez et al. 2019). Various studies showed that the analysis results with those instruments have excellent sensitivity, selectivity, and %RSD value. However, the methods require considerable energy consumption; and many of these instrumental techniques require pre-treatments, additional reagents, and

complex preparations. This is in contrast to the 12 principles of green chemistry, so creating and modifying real-time analytical methods in the form of sensors becomes an urgent need nowadays (deMarco et al. 2018).

Sensors take various approaches, generally based on the interaction between the sensor and the reagent or the analyte. Optical sensors are based on observing the interaction between the sensor and analytes that changed the color of the sensor. The principle underlying detection in optical sensors is colorimetry. Colorimetry works based on changes in wavelength and intensity when reagents and samples interact (Gilchrist and Nobbs 2017). Due to colorimetry sensor is based on the liquid-solid reaction, so the sensors always need reagents that can survive both in liquid and solid media. In addition, the sensor also requires a solid supporting material that can immobilize the reagent without reducing its activity in detection process (Mizuguchi et al. 2008).

Various matrices for optical sensors have been developed, including polymers, beads, and sol-gel with glass support materials [11–12]. However, some disadvantages of these matrix types are the need for instruments when quantifying the detection results, a complicated preparation process, a long-time synthesis process, and complicated operation procedures. The sol-gel is one of the matrices with vast

✉ Suherman Suherman
suherman.mipa@ugm.ac.id

¹ Chemistry Program, Faculty of Science and Engineering, Bojonegoro University, 62119 Kalirejo, Bojonegoro, Indonesia

² Department of Chemistry, Faculty of Mathematics and Natural Sciences, Universitas Gadjah Mada, Sekip Utara Kotak Pos 21 BLS, 55281 Yogyakarta, Indonesia

opportunities to develop considering its ease of synthesis results control (Du et al. 2013). Sol-gel would have a different yield character when synthesis precursors are varied. The ease of managing the characteristics of these results is widely used in various fields. As for sensor applications, sol-gel is expected to form silica nets capable of encapsulating reagents without leaching. The active site of the reagent remains active and does not prevent the reagent from interacting with the analytes (Shahamirifard et al. 2018a, b).

The colorimetry method could detect nickel using derived oxime functional group compounds, including α -furyl dioxime. The α -furyl dioxime has a pair of N atoms with lone pairs and can form a chelate bonding with nickel. The sensitivity level of α -furyl dioxym reaches a 1: 6,000,000 ratio of Ni to solvent (Soule 1925). This fact leads to the potential of α -furyl dioxym to be developed in the manufacture of Ni(II) metal ion sensors. The sol-gel usage as a matrix for reagent immobilization can be applied to the solid supporting media in filter paper. The data obtained is measured by the RGB value, converted into the Euclidean Distance (ED) data (Feng et al. 2011). Therefore, it is possible to create a sensor with good sensitivity and easy quantification based on the data.

Experimental Section

Material

Chemicals were analytical grade from Merck, including tetraethyl orthosilicate (TEOS), methanol (MeOH), triton X-100 as a nonionic surfactant, hydrochloric acid (HCl), standard solutions of nickel, calcium, magnesium, copper, cobalt, zinc, lead, and ammonia solution (NH₃). Distilled water was obtained from Ikapharmindo Putramas, α -furyl dioxime was from Tokyo Chemical Industry, and Whatman 42 paper was acquired from GE Healthcare.

Instrument

A scan engine (Canon CanoScan LiDE 300) was used to record the results of detection, an infrared spectrophotometer (FTIR Thermo Nicolet iS10) for determination of functional groups, and a Scanning Electron Microscope (JEOL JSM- 6510LA) for assessment of the morphology of filter paper before and after detection. All instrument⁴ ion analysis were for three-time samples replication (n = 3).

Preparation of sol-gel Matrix as a Ni(II) Ion Sensor

⁴ 2 mL of TEOS and methanol mixture were sterilized for 30 min. Later, 694 μ L H₂O, 10 drops of Triton X-100, 2 mL

of reagent α -furyl dioxime 0.1%, and 0.5 M HCl of 0.5 mL were added dropwise to the mixture. The mix was stirred for 5 h. Furthermore, 1 cm \times 1 cm filter paper was immersed in a sol solution and allowed to stand for 24 h in a room without light to occur the process of hydrolysis and condensation of sol-gel in the filter paper pores. The filter paper was drained and left for 4 days for the aging wet gel. Before use, the synthesized sensor is heated at 40 °C. All sol-gel preparation processes were analyzed by one-way analysis of variation with the number of replicates adjusted for the number of variations.

Experimental Procedure for the Determination of Nickel

A nickel analyte with a concentration of 2 ppm was prepared as much as 10 mL. 0.5 mL of 2 M ammonia solution was added to the analyte. The sol-gel membrane was dipped in the analyte for 3 min to form a color. After the sensing process, the formed color is scanned to record the color change. By using the Euclidean Distance (ED) equation, the RGB value of the color is converted to the ED value. This step was also used for real samples (river and tap water) which taken from nature that have been acid-preserved.

In this study, testing of the degree of leaching and interference were conducted as well. The degree of leaching was carried out by contacting the sol-gel membrane with aquadest, after drying it was then contacted with nickel analyte. Meanwhile, the interference test was carried out by contacting the sol-gel membrane with 2 ppm nickel solution which had been added with various interference metals. The solution mixture was first alkalized with ammonia solution before being contacted.

Results and Discussion

Effect of Variations on Preparation Parameters Towards the Performance of Sensing

Each parameter given in the sol-gel synthesis will affect the structure of the synthesis product, such as stiffness, average pore size, pore size distribution, surface area, surface polarity, ionic conductivity, silanol functional group concentration, and structural properties of xerogel (Podbielska et al. 2006). The aging time is an affecting parameter towards the structural character and mechanical strength of the synthesis results. The aging process is the stage that separates the shape of the sol into a wet gel. At this stage, there will be a change in the structure of silica from Si-OH hydrolysis to Si-O-Si (Hench and West 1990). This stage

Fig. 1 The effect of aging time on ED values

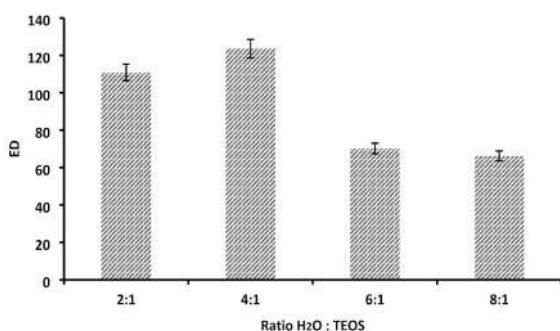
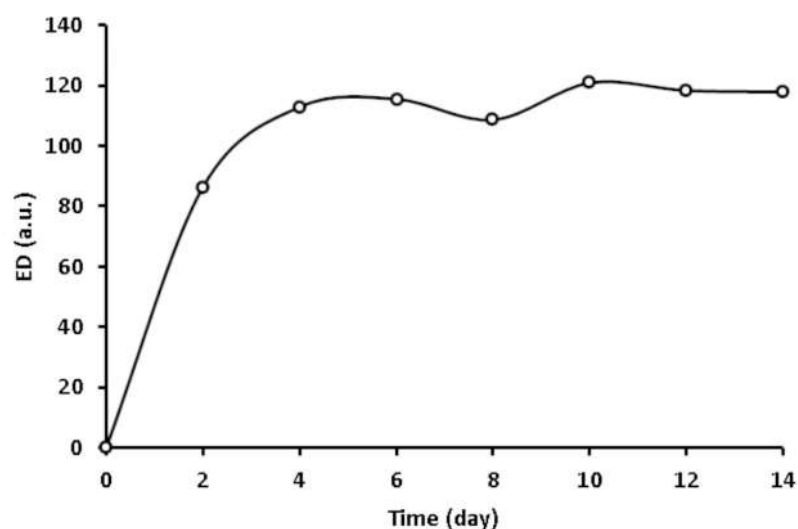


Fig. 2 The effect of water: precursor ratio on ED value

is slow and will have consequences for the length of time needed for the aging stage to complete.

Silica sol could fill the pores of filter paper. This condition is different compare to glass media that utilize interactions between glass surfaces filled with silanol groups that expect interaction between the glass surface and silica sol (Samadi-Maybodi et al. 2015). In addition, the pores of glass are also much smaller than paper, considering a physical interaction occurred. In contrast, the gel filter paper matrix that has formed Si-O-Si filled the pores of filter paper without forming chemical bonds or other interactions with the surface of the supporting media so that the aging time needed for the sol-gel with filter paper media is much shorter than the glass media that require 14 days. Fact that a gel was formed is confirmed by SEM analyses.

Figure 1 shows that there was a sharp increase in intensity immediately on the 2nd day and continued on the 4th day, and appeared constant afterwards to the 14th day. This

data shows that with paper media, sol-gel has reached a good aging time even though it is only 2 days. It is very different from sol-gel which is embedded in glass media which requires aging time up to 14 days (Samadi-Maybodi et al. 2015).

The mole ratio of water and precursor is the most critical variation variable and is very influential on the results of sol-gel synthesis (Fig. 2). Increasing the water mole ratio resulted in more compounds that will play a role in converting Si-OR to Si-OH and allowing the alkoxysilan hydrolysis process to run more optimally. In other words, an increasing amount of alkoxysilane would be hydrolyzed and implicate in a growing number of Si-OH species which continue in the polymerization stage and form Si-O-Si. The ever-increasing number of moles of water in sol-gel synthesis also affected the speed of the hydrolysis process. Increasing the mole ratio of water will affect growing porosity and specific surface area. So the 4:1 mol ratio is the optimum condition of the sol-gel matrix in immobilizing reagents that produced optimum pores by α -furfur dioximes (Dervin and Pillai 2017).

Determination of the optimum concentration is directly related to determining the maximum capacity of the matrix to encapsulate reagents. The small amount of reagent under the sensing range will decrease sensitivity, while the vast amount of reagent will stimulate the occurrence of leaching. The four variations of concentration did not affected on leaching, so it can be concluded that the sol-gel matrix had an encapsulation capacity reaching 0.1% of the added reagent (Fig. 3). The highest ED value indicated this condition.

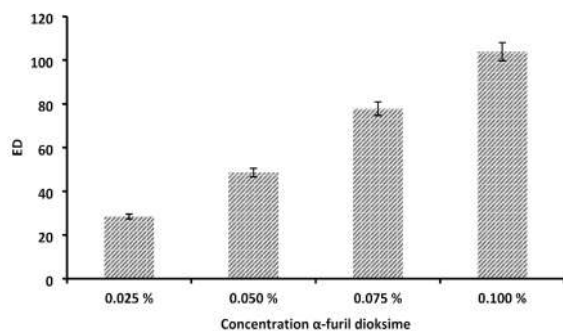


Fig. 3 The effect of reagent concentration on ED values

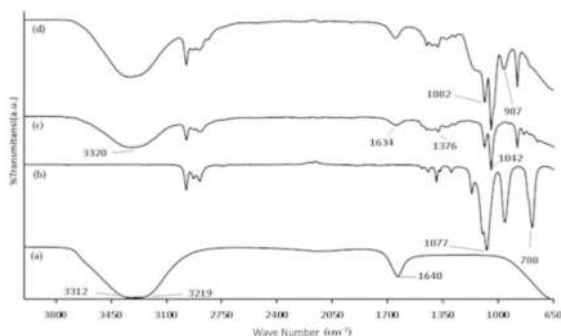


Fig. 4 IR spectra of the synthesis stage (a) H₂O (b) TEOS (c) α -furil dioxime (d) wet gel

Sensor Characterization

The FTIR spectra of H₂O showed three peaks with broad band intensity. In about 3200 cm⁻¹ there are two different peaks at 3312 cm⁻¹ and 3219 cm⁻¹, while one absorption appeared at 1640 cm⁻¹. The peak refers to asymmetric OH stretching vibrations, symmetry OH stretching vibrations, and OH bending vibrations, respectively. The IR spectra for TEOS showed several specific peaks for functional groups in TEOS compounds, such as peak at 1077 cm⁻¹ which are related to Si-O and C-O functional groups. This sharp shape of the peaks possibly due to domination of that group in TEOS compounds (Choodum et al. 2015). Meanwhile, peak at 780 cm⁻¹ related to the vibration of -(CH₂)_n. The IR spectra for the α -furil dioxime reagent possessed on 1376 cm⁻¹, 1634 cm⁻¹, 1042 cm⁻¹, and 3320 cm⁻¹, which sequentially lead to symmetry stretching C=N, asymmetry stretching C=N, C-O-C stretch vibration, and -OH stretching vibration, respectively (Egneus 1972) (Fig. 4).

The spectra of the synthesized wet gel have an absorption profile that like the α -furil dioxime spectra, especially in specific areas of α -furil dioxime, such as absorption of about 1600 and 1300 cm⁻¹. In the wet gel spectra, the sol-gel results have characteristic an absorption peak at a

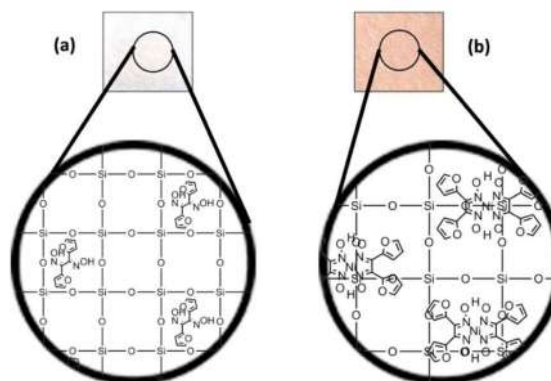


Fig. 5 Model of interaction (a) between xerogel and α -furil dioxime and (b) between xerogel and nickel- α -furil dioxime complex

wavenumber of 1082 cm⁻¹ indicating the absorption of Si-O. There is also a new peak at 987 cm⁻¹ which corresponds to Si-O-Si stretching; the intensity of these peaks was relatively small because, at the wet gel stage, the number of Si-O-Si chains formed was still relatively small. At the damp gel stage, there was no interaction between silica gel and the α -furil dioxime reagent; this was shown by the continued absorption of the active reagent groups at 1646 cm⁻¹ and 1379 cm⁻¹. So the interaction formed between the reagent and the matrix is only expected to be a physical interaction whose simulation is shown in Fig. 5.

Characterization of surface by using SEM was used to see the morphology of the filter paper of the solid supporting material before and after being coated with xerogel. As can be seen in Fig. 6a, the morphology of the filter paper has very large cavities and in Fig. 6b revealed that all cavities are covered by xerogel.

Degree of Leaching and Analytical Parameters

Determination of the degree of leaching is carried out by the twice-drying technique. Sensors free of leaching will show colors even if they have been contacted with distilled water. It means that the sensor does not lose its sensing quality due to leaching. In addition, Fig. 7 showed that the sensor surface which immersed in water first, then contacted with nickel, slightly decreased the ED value, but does not interfere with the sensing process and the difference is not detected by the eye.

The linear region will indicate the point of the concentration range resulting in the response, which is constantly increasing at the ED value obtained. Linearity data will show the y equation in Fig. 8. The y equation will also show the value of the slope, indicating the sensitivity of the synthesized sensor. While the LOD value obtained was 0.1 ppm, and the LOQ value was 0.4 ppm. These values are

Fig. 6 SEM images of Whatman 42 filter paper (a) before being coated with xerogel, and (b) after being coated with xerogel

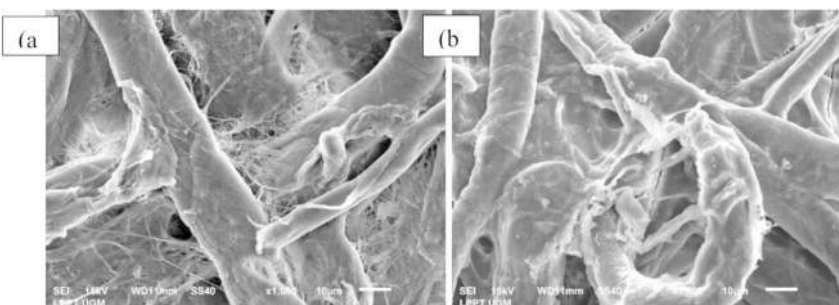


Fig. 7 Sensor leaching degree by double-dipping

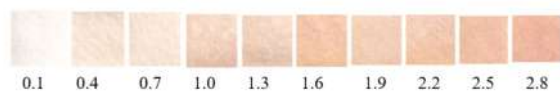
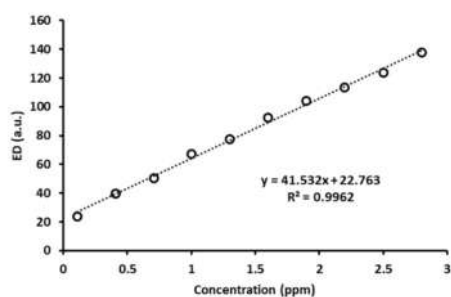
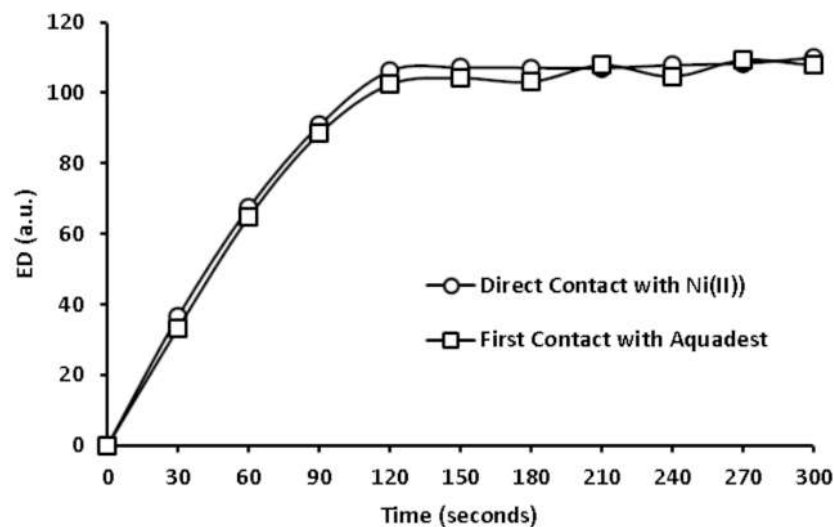


Fig. 8 Sensor standard curves and sensor color sequences

comparable with the previous results reported for nickel detection such as by modified UV-Vis method (Tokay 2017) and other methods [24–25].

The selectivity is a parameter that indicates the sensor's performance when contacted with environmental samples. Figure 9 showed that only Cr metal could significantly interfere with sensor performance among the tested metals. Based on the soft and hard acid-base theory, the metal ion of Cr(III) is classified as hard acid, and NH_3 is a hard base. Meanwhile, Ni(II) metal ion is classified as a borderline acid. Thus, NH_3 would prefer to interact with Cr(III) rather than Ni(II). However, this can be overcome by adding excess NH_3 so that there is still a Ni(II) and NH_3 complex that is formed even though Cr(III) metal is present.

Data on Fig. 9 expressed selectivity test results that the sensor can work with reasonable accuracy on environmental samples. Accuracy investigation will show the quality analysis from the proposed method, and the data is shown in Table 1. The method used to determine accuracy is spiking with 3 replications per sample. River and tap water samples have good % recovery results (which the origin concentration of nickel is around 2 ppm). Meanwhile, for the artificial samples with a concentration of 2 ppm, it is found that there

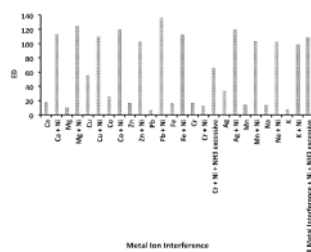


Fig. 9 Graphic for determining sensor selectivity for a variety of inter-fereent metals

Table 1 Percent recovery of the sensor for measuring water samples

Sample	%Recovery		
	1 ppm	2 ppm	3 ppm
River samples	114.57	119.54	104.08
Tap water samples	114.79	102.67	103.42
Artificial sample	114.93	95.67	75.00

is one value that is smaller than 80%. This condition possibly due to 3 ppm of concentration level already out of the linearity range, thus making the accuracy value decreased. In general, the results of accuracy validation can still work properly.

Conclusion

A sensor for the metal ion Ni(II) by the sol-gel method on filter paper media has been successfully synthesized. Preparation of sensors needed a short period through a simple process of fabrication step. The quantification process did not need any additional instruments, so the energy use in this sensor application was minimal. The sensor could detect Ni(II) ions in environmental samples. Its performance was only affected by Cr(III) ions. It has good characteristics as indicated by leaching-free, selectivity, and acceptable accuracy.

Acknowledgements Authors thank to Ministry of education, culture, research, and technology-Indonesia for their support and facilitating this research through PDUPT 2020–2021 scheme.

References

- Choodum A, Kanatharana P, Wongniramaikul W, NicDaeid N (2015) A sol-gel colorimetric sensor for methamphetamine detection. *Sens Actuators B Chem* 215:553–560
- deMarco BA, Rechelo BS, Totoli EG, Kogawa AC, Salgado HRN (2018) Evolution of green chemistry and its multidimensional impacts: A review. *Saudi Pharm J* 27(1):1–8
- Denkhaus E, Salnikow K (2002) Nickel essentiality, toxicity, and carcinogenicity. *Crit Re Oncol Hematol* 42(1):32–56
- Dervin S, Pillai SC (2017) An introduction to sol-gel process for aerogels. In: Pillai SC, Hehir S (eds) *Sol-gel materials for energy, environment and electronic applications*. Springer, Naderland
- Du A, Zhou B, Zhang Z, Shen J (2013) A special material or a new state of matter: a review and reconsideration of the aerogel. *Materials* 6(3):941–968
- Egneus B (1972) Investigations of dioximes and their metal complexes. *Talanta* 19(11):1387–1419
- Feng L, Zhang Y, Wen L, Shen Z, Guan Y (2011) Colorimetric determination of copper(II) ions by filtration on sol-gel membrane doped with diphenylcarbazide. *Talanta* 84(3):913–917
- Ghaedi M, Ahmadi F, Shokrollahi A (2007) Simultaneous preconcentration and determination of copper, nickel, cobalt, and lead ions content by flame atomic absorption spectrometry. *J Hazard Mater* 142(1–2):272–278
- Gilchrist A, Nobbs J (2017) *Encyclopedia of Spectroscopy and Spectrometry*, 3th Edition, University of Leeds UK
- Hench LL, West JK (1990) The sol-gel process. *Chem Rev* 90:33–72
- Herreros-Chavez L, Morales-Rubio A, Cervera ML, de la Guardia M (2019) Partial least squares modelization of energy dispersive X-ray fluorescence. *Talanta* 194:158–163
- Kang JH, Lee SY, Ahn HM, Kim C (2017) A novel colorimetric chemosensor for the sequential detection of Ni²⁺ and CN⁻ in aqueous solution. *Sens Actuators B Chem* 242:25–34
- Kasprzak KS, Bal W, Karaczyn A (2003) The role of chromatin damage in nickel-induced carcinogenesis. A review of recent developments. *J Environ Monit* 5(2):183–187
- Milne A, Landing W, Bizimis M, Morton P (2010) Determination of Mn, Fe, Co, Ni, Cu, Zn, Cd, and Pb in seawater high-resolution magnetic sector inductively coupled mass spectrometry (HR-ICP-MS). *Anal Chim Acta* 665(2):200–207
- Mizuguchi H, Zhang Y, Onedera H, Nishizawa S, Shida J (2008) On-site determination of trace nickel in liquid samples for semiconductor manufacturing by highly sensitive solid-phase colorimetry with α -furyl dioxime. *Chem Lett* 37(7):792–793
- Moersilah M, Siswanta D, Roto R, Mudasir M (2017) Optical chemical sensor of Cd(II) in water based on 1-(2-pyridilazo)-2-naphthol immobilized on poly(methyl methacrylate) and 2-nitrophenyl octyl ether matrix. *Malaysian J Anal Sci* 21(4):784–792
- Podbielska H, Ulatowska-Jarza A, Muller G, Eichler HJ (2006) *Sol-gels for optical sensors*. In: Baldini F, Chester AN, Homola J, Martellucci S: *Optical chemical sensors* 224, Springer, Naderland
- Salman M, Shafique U, Zaman W, Rehman R, Yousaf A, Azhar F, Anzano JM (2011) A rapid method for measurement of nickel and chromium at trace level in aqueous samples. *J Mex Chem Soc* 55(4):214–217
- Samadi-Maybodi A, Rezaei V, Rastegarzadeh S (2015) Sol-gel based optical sensor for determination of Fe (II): A novel probe for ion speciation. *Spectrochim Acta A* 136:832–837
- Shahamirifard SA, Ghaedi M, Montazerzohori M (2018a) Design a sensitive optical thin film sensor based on incorporation of isonicotilohydrazide derivative in sol-gel matrix for determination of trace amounts of copper (II) in fruit juice: Effect of sonication time on immobilization approach. *Ultrason Sonochem* 42:723–730
- Shahamirifard SA, Ghaedi M, Hajati S (2018b) A new silver (I) ions optical sensor based on nanoporous thin films of sol-gel by rose bengal dye. *Sens Actuators B Chem* 259:20–29
- Soule BA (1925) Alpha-furildioxime as a reagent for the detection and determination of nickel. *J Am Chem Soc* 47(4):981–988
- Suherman S, Hakim MS, Kuncaka A (2021) Optical chemical sensor based on 2,2-furildioxime in sol-gel matrix for determination of Ni²⁺ in water. *Processes* 9(2):280–288
- Tokay F (2017) Development of UV-Vis spectrophotometric method for rapid nickel determination in original oil matrix. *J Nat App Sci* 21(2):332–337

Wang L, Ye D, Cao D (2012) A novel coumarin Schiff-base as a Ni(II) ion colorimetric sensor. *Spectrochim Acta A* 90:40–44

Publisher's Note Springer Nature remains neutral with regard to jurisdictional claims in published maps and institutional affiliations.

Springer Nature or its licensor holds exclusive rights to this article under a publishing agreement with the author(s) or other rightsholder(s); author self-archiving of the accepted manuscript version of this article is solely governed by the terms of such publishing agreement and applicable law.

A Sol-gel Membrane Utilized Cellulose Paper Doped with α -furil Dioxime for Colorimetric Determination of Nickel

ORIGINALITY REPORT

6%

SIMILARITY INDEX

5%

INTERNET SOURCES

4%

PUBLICATIONS

1%

STUDENT PAPERS

PRIMARY SOURCES

1

katalog.hacettepe.edu.tr

Internet Source

1%

2

ir.must.ac.ug

Internet Source

1%

3

journal.ugm.ac.id

Internet Source

1%

4

Seyed Alireza Shahamirifard, Mehrorang Ghaedi, Shaaker Hajati. "A new silver (I) ions optical sensor based on nanoporous thin films of sol-gel by rose bengal dye", Sensors and Actuators B: Chemical, 2018

Publication

1%

5

www.smujo.id

Internet Source

<1%

6

cas-ir.dicp.ac.cn

Internet Source

<1%

7

Mochamad Z. Fahmi, Denika L. N. Wibowo, Yu-yu Aung, Nindayu Indrasari et al. "Nanohybrid carbon nanodots-CuFe₂O₄ as

<1%

selectively magnetofluorescent agent on tumor cells", Journal of Materials Research, 2023

Publication

8	digiresearch.vut.ac.za Internet Source	<1 %
9	www.science.gov Internet Source	<1 %
10	Biswajit Parhi, Debasrita Bharatiya, Sarat K. Swain. "Dielectric study of nanostructured ternary composite derived from amalgamated CuO/Ag ₂ O on graphene oxide sheets", Journal of Materials Research, 2023 Publication	<1 %
11	clock.uclan.ac.uk Internet Source	<1 %
12	etheses.saurashtrauniversity.edu Internet Source	<1 %
13	scholarworks.gsu.edu Internet Source	<1 %

Exclude quotes Off
Exclude bibliography On

Exclude matches Off